ABSTRACT

High conductivity is a prerequisite for any material for it to be used in the field of electromagnetics. Metals like copper and aluminium are used for a variety of electromagnetic (EM) applications in industries like electronics, communication, avionics as well as in defence owing to their high conductivity. Metals are generally used to either reflect or attenuate the EM fields. For a material to be considered for any EM application, it should have good electrical and mechanical properties and should be economically viable. Along with good electrical conductivity, high permeability and permittivity are also preferable for such materials. The mechanical properties include light weight, good strength to weight ratio, easy to fabricate and resistance to environmental and galvanic corrosion.

Polymers present an interesting alternative to metals for EM applications because of their excellent mechanical properties like good strength to weight ratio. They are easily moldable into the required geometry and are cost effective. But most of the commercially available polymers are insulating. Hence the challenge is to develop conducting polymers with good mechanical properties. There are two types of conducting polymers – intrinsically conducting polymers also known as conjugated polymers and conducting polymer composites. In the case of conjugated polymers, the polymers are intrinsically conducting. Some examples of these polymers are polyaniline, polypyrrole, polythiophenes and polyacetylene. The conductivity is achieved by virtue of their conjugated π electrons. The conductivity of these polymers can be varied from semiconducting to metal like by doping. Even though the conductivity of the doped conjugated polymers is attractive for EM applications, they have poor mechanical properties. The electrical and mechanical properties of conducting polymer composites make them suitable for EM applications. Conducting polymer composites is the other option for obtaining polymers with excellent mechanical as well as electrical properties. In this case conducting fillers like carbon, aluminium or silver are added into an insulating polymer like polyethylene, polypropylene or silicone rubber to form a conducting polymer composite. The conductivity achieved in this case is because of a phenomenon known as percolation. The polymer exhibits conductivity only beyond a filler loading called percolation threshold. The percolation threshold of a composite depends on the shape, size and conductivity of the filler, and its interaction with the base polymer. In this study, conducting polymer composites are designed for various applications like shielding, chaffing and camouflage. When a material is exposed to an EM field, three types of losses are incurred namely reflection, absorption and multiple reflection losses. The reflection loss depends primarily on the conductivity of the material; the absorption loss depends on the conductivity and the imaginary permittivity whereas the multiple reflection loss depends primarily on the thickness of the material. For a material to be used as an EM shield, the total attenuation in the material should be high. For chaffing applications, the reflection loss has to be maximum while for camouflage applications, the absorption loss has to be maximum with minimum reflection. For all those applications, the material should possess nominal dc conductivity. Hence the primary objective of this study was to improve the conductivity of the polymer. Once the high conductivity is achieved, the properties of the material can be appropriately tuned for chaffing and camouflage. The objectives of this research work can be summarized as follows. (1) Understand the effect of particle size, shape and conductivity of fillers on the electrical properties of the composites; (2) Develop a mathematical model to predict the conductivity of various types of composites, (3)

Synthesize different polymer nanocomposites and measure the shielding effectiveness of the composites using ASTM D4935 method in the frequency range of 30 MHz to 1.5 GHz; (4) Understand the factors limiting the shielding effectiveness of various composites; (5) Design a new type of composite to overcome the limitations of the traditional composites to achieve extremely high shielding effectiveness of more than 60 dB, (6) Propose a new strategy for the measurement of shielding effectiveness of composites in the frequency range up to 18 GHz, (7) Segregate the reflection and absorption loss within the shielding material so as to adapt the material developed for chaffing and camouflage applications.

In the present study, carbon-based fillers dispersed in silicone rubber polymer is used. Silicone rubber was used due to its excellent mechanical properties and ease of processing. Carbon makes excellent filler because of its high conductivity and its availability in various shapes and sizes. Carbon nanotubes, carbon nano fibres, spherical nano carbon particles and carbon micro coils are some of the forms of carbon that are commercially available. Micron sized carbon has been used in various industries to improve the mechanical properties of rubber and other polymers.

The first step to design a carbon-based conducting composite would be to choose the shape and size of the carbon filler to be used. As stated earlier, the conductivity in the case of polymer composites can be explained by percolation theory. The composites become conducting once the filler loading goes beyond the percolation threshold. Hence to synthesize a conducting polymer, the percolation threshold for different shapes and sizes has to be calculated. Various models are available for predicting the percolation behaviour of composite like statistical, thermodynamic and the geometric percolation models. Of these the statistical models are computationally intensive but they provide the flexibility to study various filler geometries. The thermodynamic percolation models emphasize the interfacial interactions between the polymer and the filler but do not study the effect of filler shape, size and orientation. Geometric models are specifically used for solid mixtures. The advantages of statistical and thermodynamic models are combined and a new Monte Carlo (MC) based method is devised for studying the percolation behaviour of the composite.

The MC method was implemented for spherical particles and fibre like particles and the percolation threshold was calculated for particles of different particle sizes. The percolation threshold was then compared with the thermodynamic Mamunya model and there was a good correlation between the two models. The model was then used to study the effect of particle diameter, aspect ratio and the distribution of particle sizes, on the percolation threshold and the conductivity of the composites. When the size of the filler particles was decreased from micron to nano, the percolation threshold is reduced. It was also seen that the percolation threshold of the composite reduced when the distribution of particle size had larger standard deviation. This could be one of the reasons for the discrepancy between the percolation values obtained experimentally and those calculated using statistical models. It was also seen that there was not much variation in composite conductivity beyond the percolation threshold for a given filler. The conductivity of the composite can be increased further if the interparticle distance between the fillers is reduced or by increasing the filler conductivity.

In the case of composites with fiber like fillers it was seen that the percolation threshold of fibres was less than that of spherical particles with the same diameter. This was because for the same filler loading, the interparticle distance is significantly reduced in fibers. The conductivity behaviour obtained using fibres was comparable to those of the spherical particles beyond the percolation threshold. The quantum tunneling of electrons was responsible for facilitating the composite conductivity. Hence from the MC studies it was concluded that, by using fibres instead of spherical particles the filler loading required to attain conductivity in composites can be significantly reduced. Increasing the filler loading beyond the percolation threshold would not be advantageous.

The polymer nanocomposites were synthesized using silicone rubber (SR) as the base polymer and multiwalled carbon nanotubes (MWCNT) or carbon nanofibers (CNF) as fillers. The size and shape of the fillers used were studied by Scanning Electron Microscopy (SEM). The mixing methodology employed included ultrasonication of the polymer- filler mixture and high temperature curing to obtain samples of different shapes and geometries. Samples with up to 4% filler loading of either MWCNT or CNF filled SR were made. The dispersion of fillers within the polymer matrix is important for a predictable performance of the nano composites. This was measured by studying the variation of filler content in different cross sections of the polymers using the Energy Dispersive X-ray (EDX). It was seen that there was not much variation in filler distribution and hence the mixing methodology was adequate to produce samples of good dispersion. Direct methods of conductivity measurement are difficult due to the nature of the composites. The composite samples have high surface resistance which can lead to problems regarding improper contact with the electrodes. The conductivity of different composites was measured using a 4 probe van der Pauw method. It was seen that both the MWCNT and CNF filled SR samples became conducting with 4% filler loading. The percolation threshold in the case of MWNCT filled SR is found to be 1.5% whereas for the CNF filled SR it becomes conducting beyond 1%. This was because of the higher aspect ratio of the CNF. Beyond the percolation threshold, both the MWCNT and CNF filled SR showed similar conductivity.

The shielding effectiveness (SE) of the samples was measured using the ASTM D4935 -2010 method. As the method is meant for samples of high surface resistance, the measurement is done as a comparison between a test sample and a reference sample made of the same material but different geometry. The frequency range of this measurement was from 30 MHz to 1.5 GHz. It was seen that the maximum shielding effectiveness was of the order of 6 dB. In the frequency range specified, the shielding effectiveness is due to the surface conductivity of the sample. The dimensions of the filler particles (< 200 μm) were much smaller than the wavelength (0.2 – 10 m) in use. The shielding effectiveness is expected to improve in the X and Ku band. Thus, the shielding effectiveness of these traditional composites is limited. This was insufficient for producing shielding materials and hence a different approach is required

From the MC studies, it was evident that the limitation in the composite conductivities was due to the interparticle distance between the fillers. The conductivity of the materials could therefore be improved if better electrical contact between different filler particles is achieved. Thus, a new method was developed for producing a new type of polymer composite namely polymer composite layered with CNF wafers. Ag- S nanoparticles were developed in the lab to bind the different CNF particles at the nano level. The CNF fibers bound by the Ag-S nanoparticles were converted into a wafer and the wafers were used for sandwiching the SR polymer filled with CNF. The SEM studies conducted on the CNF wafer produced showed that its structure was a collection of Ag- S nodes binding different CNF particles. There were lot of voids within the CNF wafer. The interaction between Ag-S nanoparticles and CNFs were due to π-π interactions. When the polymer was poured on to the CNF wafer surface, the polymer percolated into the CNF wafer matrix. This resulted in the expansion of the CNF wafer and helped in a good binding between the polymer and the CNF wafer.

The shielding effectiveness of the SR composites layered with CNF wafers was studied. It was seen that these layered composites had high SE of 60 dB, in the 30 MHz to 1.5 GHz frequency range. The SE of these composites could be improved by increasing wafer thickness or adding more number of layers or increasing the CNF loading in the composite. The SE of the composites was improved by sandwiching 2% CNF filled SR with two CNF wafers. Beyond this filler loading, the SE did not improve. When an unfilled SR is sandwiched between two CNF wafers, these wafers expand due to the percolation of SR. When 2% CNF filled SR is used, the CNF fillers in SR act as an electrical contact between wafers, but the expansion is reduced due to increased viscosity. Adding more fillers ceases the expansion and hence the SE does not improve further. The high SE of the SR composites sandwiched with CNF wafers along with the good mechanical properties make them good alternatives for shielding applications.

The shielding effectiveness of the conventional CNF and MWCNT composites, and the SR composites layered with CNF wafers were measured in the frequency range up 18 GHz. There is no standard method for measuring the SE of materials beyond 1.5 GHz. Hence a new method is devised. The measurements are based on IEEE-299 method which is actually meant for measuring the SE of enclosures in the frequency range of up to 100 GHz. The sample to be studied for SE performance is mounted in a circular hole in the cable penetration panel of an anechoic chamber. The measurements were conducted by illuminating the sample using a ridged horn antenna and SE was calculated as the difference in transmitted field in the absence and in the presence of the sample. It was seen that the shielding effectiveness of CNF and MWCNT filled SR composites as less when compared to the SR composites sandwiched with CNF wafers. The SR composite sandwiched with CNF wafers showed shielding effectiveness of more than 80 dB which make them appropriate for all shielding applications.